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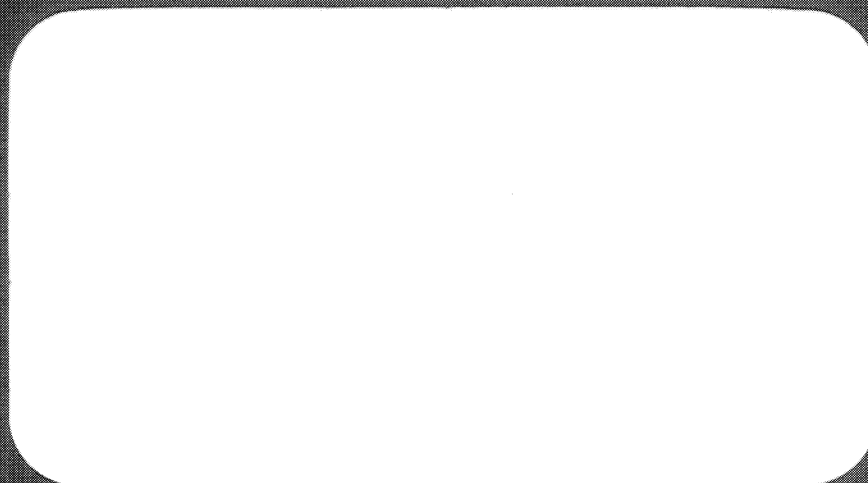
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PURIFICATION OF GEMINI FUEL CELL WATER
BY ION-EXCHANGE CHROMATOGRAPHY

National Aeronautics
and Space Administration
Manned Spacecraft Center

IIT RESEARCH INSTITUTE

Report No. IITRI-U6019-7
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PURIFICATION OF GEMINI FUEL CELL WATER
BY ION-EXCHANGE CHROMATOGRAPHY

April 13 through November 12, 1965

Contract No. NAS 9-4107
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FOREWORD

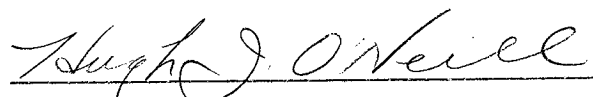
This is Report No. IITRI-U6019-7 (Final Report) on IITRI Project U6019 (formerly C6061), entitled "Purification of Gemini Fuel Cell Water by Ion-Exchange Chromatography." The work was performed by IIT Research Institute for the NASA Manned Spacecraft Center, Houston, Texas, under Contract No. NAS 9-4107. This report covers the period from April 13 through November 12, 1965. The project monitor at the Manned Spacecraft Center was Dr. W. W. Kemmerer.

Personnel who contributed to the research effort included J. I. Bregman, James Bednarczyk, Harold Combs, Joan Frerichs, H. P. Gregor, E. L. Grove, Warren Loseke, Allan Somora, W. Whaley, and H. J. O'Neill.

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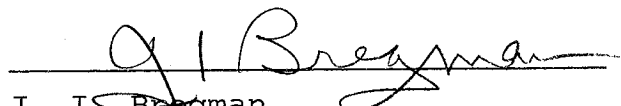
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ABSTRACT

PURIFICATION OF GEMINI FUEL CELL WATER BY ION-EXCHANGE CHROMATOGRAPHY

The objective of this program was to apply ion-exchange chromatography to the purification of Gemini fuel cell water. Thirteen selected resin beds were evaluated in both mono- and multibed combinations. Charcoal adsorbents also were screened for their removal of hydroquinones, which were responsible for the water color. However, the subsequent use of a strong-base macroreticular anion-exchange resin for the removal of sulfonic acids also performed this function quite well and therefore eliminated the need for charcoal.

The system that has the best selectivity toward the organic and inorganic constituents in the fuel cell water consists of a mixed bed of resins IRA-904, IRA-68, IRC-84, IR-45, and IR-120. Bed ratios and projected bed weights both for a nominal and an optimal bed system employing a 2.5x reliability factor are reported.

During the latter portion of the program, the Sim-5 water sample was employed in the column evaluation studies. Sim-5 was the most heavily contaminated sample encountered during the program. The most critical factor in the development of an efficient purification system is the gross variation in the nature of the fuel cell effluent.

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PURIFICATION OF GEMINI FUEL CELL WATER
BY ION-EXCHANGE CHROMATOGRAPHY

I. INTRODUCTION

The objective of this program was the development of an ion-exchange purification procedure to render Gemini fuel cell water suitable for drinking by astronauts. The purified water should exhibit the following properties: specific conductance, 6 μ mhos; pH, 6 to 8; total organics, 40 ppm; color, 15 units; turbidity, 5 units; odor threshold number, 1; and taste threshold number, 1. The water should meet USPHS standards in all respects not mentioned above. Other environmental requirements include: weight of resin bed, <1 kg; flow rate, 1.4 lb/hr; total volume (of water), 27 gal; effective operation at temperatures from 32 to 160°F; and ΔP , <0.5 psi at termination of the run. The final resin bed should consist of two separate units.

Because the progress reports on this project contained detailed descriptions of our experimental work, this report briefly reviews our early studies and concentrates on our studies with the "worst case" sample, Sim-5.

II. PRELIMINARY SCREENING STUDIES

A. Water Samples

In the initial studies both cationic and anionic ion-exchange resins were screened to determine which beds exhibited the greatest selectivity toward the removal of the organic and inorganic contaminants in the fuel cell effluent. For these screening studies, a pooled water sample was prepared from 16 of the 25 original water samples supplied to us by the Manned Spacecraft Center. These samples were pooled on the basis of their specific conductance, pH, and color. The total volume of this pooled sample was 15.1 liters.

Emission spectrographic analysis of the pooled sample indicated that its major cation contaminants were titanium, aluminum (6.0 ppm), calcium (6.1 ppm), magnesium (16.7 ppm), and iron (0.5 ppm); the minor contaminants were copper (0.2 ppm), silicon, zinc, strontium, manganese, and chromium. Low levels of platinum were found in later samples.

Wet chemical analyses of the pooled water sample indicated that the anionic contaminants were SO_3^- (3.85 ppm), SO_4^- (46.1 ppm, without organic decomposition; total SO_4^- , 227.5 ppm, Cl^- (20.4 ppm), and PO_4^{3-} (0.07 ppm). The overall characteristics of the pooled sample as well as those of the other original water samples submitted for screening are listed in Table 1.

Table 1
CHARACTERIZATION OF FUEL CELL WATER SAMPLES

Sample	Specific Conductivity, μ mhos/cm	pH	Color	Residue, ^a ppm		
				Inorganic	Organic	Total
Pooled water	1900	2.3	70+	50	1010	1060
No. 67	1667	2.6	70+	75	701	766
No. C-1	1583	2.4	70+	2	1919	1921
No. S-1	357	3.2	15+	120	243	363
F-3	4490	2.3	70+	938	1602	2540
Sim-5	4545	2.0	70+	333	2289	2622

^aThese values were obtained by evaporating the water sample at 103°C for 1 hr and weighing the sample to determine the total residue. Then the volatile organic material was removed by placing the sample in a muffle furnace at 600°C for 10 min. The inorganic residue was weighed directly, and the organic residue was determined by calculating the difference.

B. Resins

For the resin screening studies a standard volume of 75 ml of reagent in a 10.5 x 0.5-in. column was used. The resins were packed in the column with triple-distilled water, which was subsequently passed over a 4-ft bed of Amberlite MB-3. Both mono- and dual-bed systems were screened in order to systematically survey optimum anion-cation combinations. Of the resins screened, the IRA-68/IRC-84 combination yielded the most effective system for removal of both organic and inorganic constituents. Therefore this dual-bed system was singled out for more detailed evaluation. The various resins screened in this initial study are listed in Table 2.

C. Charcoals

Several charcoals were evaluated concurrently with the ion-exchange resins in order to compare their ability to remove and retain organic material. Retention of hydroquinone structures was of particular interest, since this material was in most cases responsible for the color associated with the water samples. Gas-chromatographic analyses of the trimethylsilyl ethers of the three hydroquinones considered most likely to be present (hydroquinone, t-butyl hydroquinone, and 2,5-di-t-butyl hydroquinone) confirmed the presence of hydroquinone only in the fuel cell water. Its concentration varied from about 50 to 100 ppm in the various water samples analyzed, but could not be directly correlated with the overall quality of the water.

Table 2

IDENTIFICATION OF ION-EXCHANGE RESINS

Ionac A310 is an aliphatic polyamine weak-base organic resin in the salt form (Ionac Chemical Co.).

Dowex SBR is a technical-grade, strong-base anion resin in the hydroxyl form (Nalco Chemical Co.).

Rexyn RG-50 is an organic strong-acid cation exchanger in the hydrogen form. It is a sulfonated polystyrene copolymer. It is of medium porosity and has the RSO_3^- active group (Fisher Scientific Co.; Mfg. Chemists, Fairlawn, N. J.).

Rexyn RG-1 (OH^-) is a strong-base organic anion exchanger. It is a polystyrene alkyl quaternary amine in the hydroxyl form. It is of medium porosity with the R_4N^+ active group (Fisher Scientific Co.; Mfg. Chemists, Fairlawn, N. J.).

Amberlite MB-3 is a dyed mono-bed resin, that is, an intimate mixture of Amberlite IR-120 in the hydrogen form and Amberlite IRA-410 in the hydroxyl form. The resin is dyed with an indicator that changes from deep blue-green to yellow as the deionizing capacity of the resin is exhausted (Rohm & Haas).

Amberlite MB-1 is a specially prepared mixture of Amberlite IRA-400 (hydroxyl form) and Amberlite IR-120 (hydrogen form) suitable for immediate use in mono-bed operations (Rohm & Haas).

Amberlite IRA-68 is a synthetic, weakly basic anion-exchange resin containing only tertiary amine functional groups in a spherical bead form that has been made highly porous. In addition to a high exchange capacity, this resin is reported to exhibit both outstanding chemical and thermal stability (Rohm & Haas).

Amberlite IRA-93, a macroreticular weak-base anion-exchange resin based upon the styrene divinylbenzene structure, has been demonstrated to have the attributes of an ideal weak-base anion exchanger (Rohm & Haas).

Dowex HCR-W is a technical-grade cation-exchange resin in the hydrogen form. It has an indicator that is green when new and blue when exhausted (Nalco Chemical Co.).

Dowex SAR is a technical-grade ion-exchange resin in the hydroxyl form. It is a strong-base anion resin (Nalco Chemical Co.).

Amberlite IRC-84 (formerly Amberlite X-232) is a weakly acidic (carboxylic) cation-exchange resin that is considerably less acidic than Amberlite IR-120, but slightly more acidic than Amberlite IRC-50 (Rohm & Haas).

Dowex A-1 is a chelating resin that consists of a styrene divinylbenzene copolymer with the imino diacetate grouping. It is supplied in sodium form (Dow Chemical Co.).

Amberlite IRA-904 is a strong-base macroreticular anion-exchange resin of the tertiary amine class. It is supplied in the chloride form. It is reported to be highly resistant to chemical and physical degradation (Rohm & Haas).

For instance, the Sim-5 and P-3 water samples, which were the most highly contaminated, were the same two samples that represented the high (91 ppm) and the low (56 ppm) hydroquinone values.

The Barnebey-Cheney grade PL charcoal adsorbent exhibited the greatest retention (200 mg/g) of the 13 charcoal products screened. The Barnebey-Cheney grades 557 and SK were second in effectiveness and exhibited identical retention capacities of 175 mg/g. The remaining charcoal beds exhibited retention capacities in the range of 5 to 140 mg/g.

At this point it appeared that a combination of the IRA-68/IRC-84 bed and grade PL charcoal would be sufficient for the purification procedure. A backup bed would probably be required, mainly for final pH adjustment. In his studies, Dr. Kester of McDonnell Aircraft used a IRC-50/IRA-68 mixed bed (7:3); this system served his purpose very well.

D. "Worst Case" Samples

Two water samples (P-3 and Sim-5) that were received in August were much more heavily contaminated than any water previously encountered. The decrease in quality of this water was attributed to the incorporation of a new P-3 type membrane into the fuel cell. The data in Table 1 show the gross differences between these two samples and the earlier samples. Since the Sim-5 sample was considered typical of the water to be encountered in future fuel cell operation and since it resisted purification by the IRA-68/IRC-84/grade PL charcoal purification

system, all effort was redirected toward the cleanup of this "worst case" sample.

To establish the cause of the failure of the ion-exchange system for these samples, we attempted to determine the differences in the structure of the organic material. The breakthrough of organic material could not be attributed solely to its increased concentration (2.3x), since a proportional increase in bed volume did not give adequate organic retention. In order to characterize the organic residue without gross chemical or thermal alterations, a sample of the original water and several of the column effluents were lyophilized for 12 hr. The white, fluffy solid product was then analyzed by infrared, ultraviolet, and wet chemical techniques.

In general, wet chemical and emission spectrographic analyses indicated the same cation distribution found in earlier samples, with only the quantities being greater. On the other hand, the organic components exhibited a substantial difference, which was attributed mainly to a twofold increase in the calculated degree of sulfonation of the isolated polymer fragments. Of curious concern was the fact that qualitatively the infrared spectra of both the influent and effluent organic material were essentially identical and exhibited a typical aromatic disubstituted sulfonic acid spectrum. An absorption band at approximately 1410 cm^{-1} suggested the possible presence of either a carboxylate ion ($-\text{CO}_2^-$) or the grouping $-\text{CH}_2-\text{CO}-$. Both structures would be possible candidates as a result of oxidative degradation

of polystyrene. The former structure does not seem too probable at the strongly acidic pH of the water.

However, the presence of the latter structure could be further substantiated by the presence of a methylene asymmetric stretching vibration at 2930 cm^{-1} .

The first approach in cleaning up the Sim-5 sample was directed toward studying the effect of a chelating resin, Dowex A-1, since it seemed likely that a nondissociable complex could be formed that would clear the resin bed. The Dowex A-1, a chelating resin employing the imino diacetic acid functionality, exhibited an enhanced affinity for removing the organic material; however, its thermal stability and shrinkage properties, when converted to the H^+ form, were of concern. Also, the infrared spectrum of the synthesized calcium salt of o-sulfobenzoic acid did not correlate sufficiently with that of the organic residue to justify further studies of the Dowex A-1 resin. However, this finding does not rule out the possibility that other closely related salt complexes may be present.

The possibility that organic breakthrough was due to leakage of larger organic molecules was also considered, since Dr. Kester had observed that the bulky dodecylsulfonic acid (DDSA) leaked through his resin columns, while the smaller p-toluene sulfonic acid (TSA) was retained somewhat longer. Exhaustive capacity studies for both DDSA and TSA on IRA-68 showed that different leakage rates were obtained for both materials, even though bed exhaustion was not achieved. Titration data revealed

that bed exhaustion was not responsible, since organic leakage for DDSA occurred before 5% of the available milliequivalent capacity of the resin was expended.

These findings prompted the search for another resin that had suitable stability requirements and exhibited good retention properties for organic material. Therefore a macroreticular resin, such as IRA-904, was an obvious consideration even though its stability was based on its use in the chloride form. Subsequent column studies indicated that this resin had an exceedingly good holding capacity for organic material. Therefore the IRA-904 resin was evaluated further for incorporation into our original resin bed system. Section III describes these studies.

Of particular concern during this study was the variation in composition among the later fuel cell water samples and the possibility that a purification system would be developed for a water supply that is not truly representative of actual flight water. However, in order to pursue the development of an operational purification system, all studies during the latter part of the program were oriented toward the purification of the Sim-5 water.

Last month's report (Report No. IITRI-U6019-6) discussed some preliminary data on the properties of the five water samples (B series) collected from the ground power profile run conducted at McDonnell Aircraft during the last GT-5 orbital flight. At that time no information was available on the actual percentage of the total fuel cell output that each of the five

samples represented. For the purposes of calculation, we had assumed that each of the five samples represented equal proportions of the total (20%). Dr. Kester recently confirmed that this assumption was correct; therefore the calculations reported are justified.

III. PURIFICATION OF SIM-5 SAMPLE

Several columns were prepared in order to determine the resin bed requirements for purifying the "worst case" fuel cell water, Sim-5. As stated in Section II, the dual-bed IRA-68/IRA-904 system was the most suitable anion system for removal of both sulfonic acids and total organic material.

Although the IRA-68 performed exceedingly well for smaller anions, it was not suitable alone since its holding capacity for larger organic material is relatively low. On the other hand, the macroreticular IRA-904 was unsuitable alone for the opposite reason: it leaked smaller anions and had a markedly increased capacity for holding the larger organic molecules. The combination of both beds, however, exhibited excellent properties for total anion removal.

One problem associated with the IRA-904 resin is that its use in the chloride form is required. In general, resin beds should be maintained in the H^+ or OH^- form to minimize the clean-up procedure and to ensure that the purified effluent picks up water only from the bed system. The stability and holding capacity of IRA-904 in the chloride form, however, are exceedingly superior to those of other resins in any form; thus it became necessary to make an exception. Other problems are encountered with IRA-904 when it is used in the free base (tertiary amine) form: a decrease in chemical and thermal stability and an unpleasant fish-like amine odor, which can be

passed along to the effluent water. For these reasons we employed the resin in the chloride form and inserted a chloride scrubber in the final clean-up bed.

In order to determine the ratios and the positions in which the IRA-68 and IRA-904 resins should be used, four small-scale runs were made with the Sim-5 sample. In runs 1 and 2 the two columns contained the IRA-68 and IRA-904 resins in ratios of 1:4 and 1:2, and the total bed volume was 15 ml. In runs 3 and 4 the same resin ratios were employed, but their position in the bed was reversed. The effluent water was collected in 2-ml aliquots at flow rates of 1 to 2 ml/min in all four runs. Since the main objective was to determine what bed orientation and ratio were best suited for organic retention, the fractions were monitored intermittently to determine the organic breakthrough point and the pH.

The resulting fractions were analyzed for total organic materials by the ultraviolet technique, pH, color, and chloride content. The latter procedure was incorporated as a standard screening method late in the program in order to determine the contribution of the IRA-904 to the total chloride level of the Sim-5 effluent and to determine the amount of backup resin required for its removal. The specific conductance and inorganic content were not of prime interest in these runs, since they would be evaluated with respect to our final clean-up bed.

The results of these runs are presented in Table 3. The data clearly demonstrate the advantage of using the IRA-904 as the fore bed for initial organic removal. The increased chloride content of the IRA-904 effluent apparently did not affect the ability of the IRA-68 to remove either organic sulfonic acid or inorganic sulfate species, as indicated by its uniform pH control. In runs 1 and 2, after the initial organic breakthrough in fractions 5 and 6 the effluents dropped rapidly to a pH of 4.65 and held this value through fraction 16 (not shown in Table 3). In runs 3 and 4, a pH of 7.9 was maintained throughout fraction 16 (32 ml). Based on the initial Sim-5 concentration, the organic leakage of fraction 8 in run 3 was only 3.8%, as compared with the 18% leakage in fraction 5 of run 1 or the 23.8% leakage in fraction 6 of run 2. In run 1, the early breakthrough of organic material occurred at a total influent volume of only 10 ml. Based on the original Sim-5 sample, this volume amounted to a total titratable acid concentration of only 0.187 meq for the 10-ml sample. This value is far below the available milliequivalent capacity of the resin.

However, the holding capacity of the anion resins for organic material, and especially that of the macroreticular resins, cannot be directly calculated on the basis of milliequivalents of available exchange sites. This value is limited solely to the small anions, which can diffuse freely throughout the resin matrix. A more appropriate and realistic value

Table 3

RESULTS OF PRELIMINARY SCREENING OF ANION RESINS COLUMN BED^a

Run No.	Column	Effluent Fraction (2 cc)	Organic Residue, ^b mg/2 cc	pH
1	IRA-68/IRA-904 (1:4)	1	0.0434	6.7
		2	—	—
		3	0.0112	6.6
		4	0.2340	6.8
		5	0.830	7.0
2	IRA-68/IRA-904 (1:2)	1	0.0042	6.5
		2	—	—
		3	0.0048	7.0
		4	0.0678	6.8
		5	0.4042	7.2
		6	1.0942	7.0
3	IRA-904/IRA-68 (4:1)	1	0.0112	6.5
		2	—	—
		3	0.0074	6.8
		4	0.0068	7.7
		5	0.0460	7.8
		6	0.0474	8.1
		7	0.1038	8.2
		8	0.1982	8.2
4	IRA-904/IRA-68 (2:1)	1	0.0452	7.0
		2	—	—
		3	0.0100	7.3
		4	0.0074	7.6
		5	—	—
		6	0.0138	7.9
		7	—	—
		8	0.1736	8.0

^aAll columns were prepared to a total bed volume of 15 ml. Sim-5 was used as an influent at a flow rate of 1 to 2 ml/min.

^bOrganic residue was monitored by ultraviolet absorption at 255 mμ. The specific extinction value (K = 5.29) was based on the organic residue (2.359 mg/cc), which was determined by the oven procedure.

would be a definition of resin capacity in terms of weight per unit volume (mg/ml) of resin. In all probability this value will be extremely specific for the nature of the organic species being removed and therefore would be applicable only if the nature of this material remains constant. Unfortunately, for the purposes of our calculations, we must accept this assumption in order to be able to determine optimal total bed capacities. These calculations will be meaningful if future water effluents of the fuel cell are basically similar to the Sim-5 sample. If, however, any additional changes or alterations are incorporated into the fuel cell, particularly with respect to membrane structure or power loading, these same calculations, as well as the resin bed purification system itself, could become completely meaningless.

Another run was made to confirm the small-scale data and to collect large effluent fractions (4 cc). These quantitative data on organic residue and chloride, sodium, calcium, and magnesium content could then be used for preparation of the final clean-up bed. In this run (5) the bed characteristics were the same as those in run 4, but the column contained twice the amount of total resin (30 ml). The overall procedure was essentially identical to that for runs 1 through 4.

The results are presented in Table 4. These data closely parallel the data for run 4 (Table 3). In addition, a somewhat improved retention for organic material is shown. For example, as shown in Table 4, the breakthrough of organic material

Table 4

CHARACTERIZATION OF ANION RESINS IRA-904 AND IRA-68
FOR FINAL BED EVALUATION^a

<u>Fraction (4 cc)</u>	<u>Organic Residue,^b mg/4 ml</u>	<u>pH</u>	<u>Chloride,^c meq/liter</u>	<u>Specific Conductivity, μmhos/cm</u>	<u>Color</u>
1	0.0152	6.7	5.4	55.5	0
2	0.0152	6.9	4.1	55.5	0
3	0.0112	6.9	3.5	55.5	0
4	0.0180	7.0	4.7	71.4	0
5	0.0300	8.1	6.8	83.3	0
6	0.0224	8.2	5.9	62.5	0
7	0.0340	8.5	8.6	35.6	0
8	0.0340	8.6	7.8	71.4	0
9	0.0340	8.7	5.2	51.2	0
10	0.1224	8.7	9.2	50.0	0
11	0.4812	8.7	9.2	62.5	0
12	0.7820	8.6	11.1	167	0
13	0.7892	8.6	10.3	100	0
14	0.7892	8.6	12.7	50	0
15	0.8796	8.6	12.7	100	0
16	0.9172	8.6	12.4	100	0
17	0.9248	8.6	10.6	125	0
18	0.8496	8.6	11.7	111	0

^aThe column consisted of 30 ml of resin at a ratio of 2:1 IRA-904/IRA-68. The influent water was new Sim-5 at a flow rate of 2.5 ml/min.

^bOrganic residue (2.359 mg/ml) was calculated on the basis of a specific extinction coefficient of 5.32 at 255 mμ. The total organic residue was determined by the oven technique.

^cChloride analysis was determined by the mercuric nitrate procedure given in "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 10th ed., p. 61, 1955.

occurred at fraction 10 for 40 ml of influent per 30 ml of resin. The total organic holdup at this point amounts to 94 mg/30 ml of resin, or 3.1 mg/ml. Of the total organic material introduced onto the column, 99.6 wt. % was withheld. Through fraction 18, a total of 72 ml of effluent was collected, and the total organic holdup was 96.0 wt. %, which amounts to 54.4 mg of organic material per ml of the total anion resin bed. In addition, there was no evidence of color breakthrough up to this point. The restrictions imposed by the limited supply of Sim-5 water did not permit continuing this run.

The calcium, magnesium, and chloride contents of the initial Sim-5 influent were 0.90, 0.31, and 5.65 meq/liter, respectively. The combined effluent sample, through fraction 18, contained 0.39 meq/liter calcium, 0.53 meq/liter magnesium, and 8.4 meq/liter chloride. The sodium content of this effluent was 0.41 meq/liter. These data are summarized in Table 5.

Since emission spectrographic analyses showed that calcium and magnesium represented the major portion of the divalent and heavy metal cations, the level of the IRC-84 was established from these values. Since the IRC-84 will preferentially retain calcium and magnesium and leak sodium ions, IR-45 resin is also required. Thus, to calculate the amount of IR-45 resin to be used for final pH adjustment, the concentrations found for sodium were used. The quantity of IR-120 anion backup resin was estimated from the effluent chloride

Table 5

PROPERTIES OF SIM-5 WATER
BEFORE AND AFTER ANION CLEANUP^a

<u>Properties</u>	<u>Sim-5</u>	
	<u>Influent</u>	<u>Effluent</u>
Specific conductivity, μ mhos/cm	4166.6	78.2
Color	70+	0
pH	2.1	8.2
Organic content, mg/72 ml	169.8	6.8
Calcium, meq/liter	0.81	0.29
Magnesium, meq/liter	0.31	0.53 ^b
Chloride, meq/liter	5.65	8.4 ^c
Sodium, meq/liter		0.41

^aThe resin bed consisted of 30 ml of IRA-904/IRA-68 (2:1).

^bThe increased magnesium concentration was due to contamination by the resin bed. In earlier runs calcium also was shown to be removed from this bed, even after exhaustive prewashing.

^cThe increased chloride value was due to the chloride form of IRA-904 that had to be employed.

level, which was increased to a large extent over the original concentration by the contribution of the IRA-904 fore bed.

To check these calculations for an operational resin bed system, a final column was prepared. The resins IRA-904, IRA-68, IRC-84, IR-45, and IR-120 were used in the ratio of 8:4:2:1:1. The total volume of the IRA-904/IRA-68 anion bed was 60 ml, or twice that of run 5. The column dimensions were 1.9 x 20 cm. Since the exchange capacity of the IRC-84 resin is 1.6 meq/ml, theoretically, less than 1 ml of resin would be required to remove the total level of calcium and magnesium (0.059 meq/72 ml). For this study, however, the use of volumes less than 10 ml would not be representative of a large-scale run, since the bed depth for the levels required would be considerably less than the bed diameter. Thus the minimum bed depth for any resin was 10 ml.

A mixed bed of IR-45 and IR-120 (1:1) was also employed at a total bed volume of 10 ml, although the 5-ml quantity of IR-120 (1.7 meq/ml) was more than necessary for the removal of the low level of sodium (0.03 meq/72 ml) and the other monovalent anions. The quantity of IR-45 necessary for chloride removal (0.60 meq/72 ml) would also be less than the 5 ml of bed at its equivalent capacity of 2.0 meq/ml. The pertinent data regarding this run are presented in Table 6.

On the basis of organic holdup, a total of 98.9% was retained by the resin system for the 72 ml of influent water. Since this bed volume represents twice the previous bed volume,

Table 6

CHARACTERIZATION OF MULTIBED COLUMN^a
FOR PURIFICATION OF SIM-5 WATER SAMPLE

Fraction (4 cc)	Organic Residue, ^b mg/4 cc	pH	Chloride, ^c meq/liter	Specific Conductivity, μ mhos/cm	Color
1	0	6.4	4.37	19.6	0
2	0	6.2	4.07	6.2	0
3	0	6.2	4.79	62.5	0
4	0	6.4	4.65	50.0	0
5	0	6.4	4.79	52.6	0
6	0	6.4	4.51	50.0	0
7	0	6.1	5.07	50.0	0
8	0	6.3	4.93	40.0	0
9	0.0118	6.3	5.36	41.6	0
10	0.0165	6.3	5.07	29.4	0
11	0.0397	6.2	5.64	41.6	0
12	0.0530	5.8	5.36	41.6	0
13	0.0828	5.8	4.93	55.5	0
14	0.1291	5.6	4.93	58.8	0
15	0.2251	5.2	4.93	40.8	0
16	0.2715	4.9	4.79	41.6	0
17	0.4635	4.7	4.79	41.6	0
18	0.5761	4.4	4.23	35.7	0

^aThe resin bed consisted of IRA-904/IRA-68/IRC-84/IR-45/IR-120 in a ratio of 4:2:1:1:1. The column was 1.9 x 20 cm and had a total volume of 80 ml of resin; the flow rate was 2.5 ml/min.

^bThese values for organic residue are based on ultraviolet procedure using the 255-m μ absorption band. The specific extinction value is based on organic residue obtained by the oven technique.

^cThe chloride content of the distilled water passed through MB-3 was 2.82 meq/liter. A prewash of the column using this same water had an effluent level of 4.51 meq/liter.

however, this organic retention value was expected to be high. For twice the influent volume, the value would probably be closer to 95%. The organic residue weight obtained for this total effluent sample by employing the ultraviolet spectrophotometric technique (Table 6) was 25.9 ppm. The actual residue value obtained for a recombined total effluent sample by using the oven procedure was 31 ppm, while the value for the inorganic residue was 20.0 ppm. The resulting calcium, magnesium, and sodium levels for the total effluent were 0.03, 0.04, and 0.19 meq/liter, respectively. Also, in all the column runs employing the combination bed of IRA-904 and IRA-68 there was no evidence of color breakthrough nor any odor or identifiable taste associated with this product.

The decrease in pH in the later fractions (Table 6) was unexpected and suggests the use of a stronger anion base resin in the final mixed bed for pH adjustment. We used the IR-45 instead of the stronger-base anion resin R-410 (normally incorporated into the MB-1 or MB-3 mixed resin) because of its increased temperature stability (212°F). The maximum temperature recommended for most of the strong-base anion-exchange resins in the hydroxyl form normally ranges between 105 and 140°F. Since both time and the quantity of the Sim-5 sample limited studies on the effects of increased bed temperature (160°F) on the column operation and efficiency, it was preferred to screen the most temperature-stable resin systems. Also, the overall stability characteristics of the IRA-904 are better

than those of the other available macroreticular anion resins.

If, however, other resins such as IRA-911 were equally temperature stable and exhibited comparable organic retention properties, they would be preferred since the need for final chloride scrubbing would be eliminated. This would serve to both reduce the final total bed weight and remove the possibility of altering the efficiency of the IRA-68 backup bed. In Section IV the actual weight distribution of the various resin beds required for the final purification system is discussed on the basis of the data presently available.

IV. WEIGHT DISTRIBUTION OF VARIOUS RESIN BEDS

The specific requirements of a functional ion-exchange purification system for the Gemini fuel cell water are based on the assumption that the Sim-5 sample is representative of the water to be produced during future flights. Consequently, with a total organic residue of 2359 ppm, a total of 241 g of organic material will be present in 27 gal (102.2 liters) of unpurified cell water. In order to accommodate this quantity of water and to maintain a 95% organic holdup on the column, a minimum volume of 4241 ml of the IRA-904/IRA-68 bed would be required. On the basis of an average totally immersed bed density of 1.07 g/cc, the total minimum weight of the dual anion resin alone would be 4538 g. This value alone greatly exceeds the total bed weight of 1.0 kg initially strived for in purifying this water. However, this 4.5-fold increase in weight can be attributed, at least in part, to the 2.4-fold increase of organic material in the Sim-5 sample.

A further complication is that the very nature of the organic material is so different (more highly sulfonated) that larger quantities of resin per unit weight of organic material are required. If the anion resin fore bed weight were rigidly set at 1 kg, only 23 liters of the Sim-5 water, or approximately 22% of the desired water output, could be accommodated. At the 95% level of organic holdup, the final water volume of 27 gal would have a calculated organic residue of about 118 ppm.

In addition to the dual-bed anion resin weight, three backup beds must also be considered. Based on the analysis of the calcium and magnesium in the effluent water from the anion fore bed (Table 5), the total cation concentration would be 84 meq/27 gal. By allowing for these and other cations of the divalent and heavy-metals groups, the final minimum bed weight for IRC-84 would be approximately 25 g when the density of the completely immersed bed is 1.19 g/cc. The actual wet density of this resin in the shipped form, as well as of the other resins described herein, ranges from 0.67 to 0.77 g/cc. The values for the water-immersed resins were used in these calculations, because it was assumed that the ion-exchange cartridge would be incorporated into the vehicle in this "activated" form. For comparison, Table 7 lists the resin bed weights for both forms.

The requirements for the final mixed bed are somewhat less definitive since the pH values during the multibed column run (run 5, Table 6) decreased to 4.4 before a 96% organic holdup was attained. We planned to maintain the pH between 6.2 and 7.0 throughout this run, at least until the organic leakage was maintained at less than 5%. The final pH could be more efficiently controlled either by incorporating the Amberlite MB-1 or more appropriately by varying the ratio of the IR-120/IR-410 components. The temperature limitation of IR-410 (140°F) discouraged its use in this system, as mentioned previously. Based on the effluent analyses reported in Table 5, approximately 24 g of IR-120 and 445 g of IR-45 would be required for an effective

Table 7

SUMMARY OF WEIGHTS OF WETTED AND IMMERSED RESINS

Resin	Form	Capacity, meq/ml	Density, g/cc		Resin Weight, ^a g			
			Wetted ^c	Immersed ^d	Minimum Quantity		Maximum Quantity ^b	
					Wetted	Immersed	Wetted	Immersed
IRA-904	Cl	0.7 ^e	0.73	1.08	2064	3054	5161	7636
IRA-68	OH	1.6 ^e	0.74	1.06	1046	1499	2615	3747
IRC-84	H	4.0	0.72	1.19	15	25	38	63
IR-45	OH	2.0	0.67	1.05 ^f	284	445	710	1113
IR-120	H	1.9	0.77	1.10	<u>17</u>	<u>24</u>	<u>42</u>	<u>61</u>
Total					3426	5047	8566	12620

^aThe resin weights are based on a total water volume of 27 gal.

^bThese values are based on a 2.5x increase in the total resin weight according to minimum resin requirements.

^cWet density is based on resin in shipped form.

^dImmersed density is based on total water-immersed resin.

^eThe capacity is based on 54 mg/ml of organic holdup through fraction 18 (Table 2) in a bed ratio of 2:1 IRA-904/IRA-68.

^fThe density was calculated in the laboratory in a 100-ml graduate.

clean-up bed. Therefore, based on the minimum resin weights only, a final bed would consist of about 3400 g of wet resin or 5000 g of totally immersed resin. The total resin bed, incorporating a 2.5-fold weight increase as a reliability factor for all beds in the wet form, would amount to 8.5 kg.

At a total organic leakage rate of 5%, the calculated organic residue value for the final water sample would be approximately 118 ppm. In order to reduce this value to 40 ppm (the desired limit), the organic leakage value must be reduced proportionately. Since in actual operation the water will be purified under dynamic or continuous rather than intermittent or batchwise conditions, each increment of water would have to be maintained below a 1.7% leakage level. This is due to the fact that the later column effluents will not be diluted with the better-quality water formed during the early life of the bed. To maintain the organic leakage rate at the 1.7% level throughout the entire operation of the ion-exchange column, almost twice the initial quantity of the anion fore bed resin would be required. As shown in Table 4, this low leakage requirement is met only through fraction 10.

This limitation is even more demanding because of the effect of the generation rate, or occurrence, of the organic material on the overall fuel cell operation. Results of analyses performed on the fuel cell water output from the simulated GT-5 power profile run are given in Table 8 and their titration curves presented in Figure 1.

Table 8
CHARACTERIZATION OF POWER PROFILE WATER SAMPLES

Sample No. ^b	pH	Color	Specific Conductivity, μ mhos/cm	Residue, ^a ppm		
				Inorganic	Organic	Total
B-1	1.75	70+	8,197	622	2645	3267
B-2	2.30	70+	3,333	93	1475	1568
B-3	2.45	50+	2,137	104	936	1040
B-4	2.63	40+	1,449	138	917	1055
B-5	2.68	20+	1,250	122	538	660

^aValues represent average of duplicate determinations.

^bEach sample represents equal percentage (20% by volume) of the the total fuel cell output.

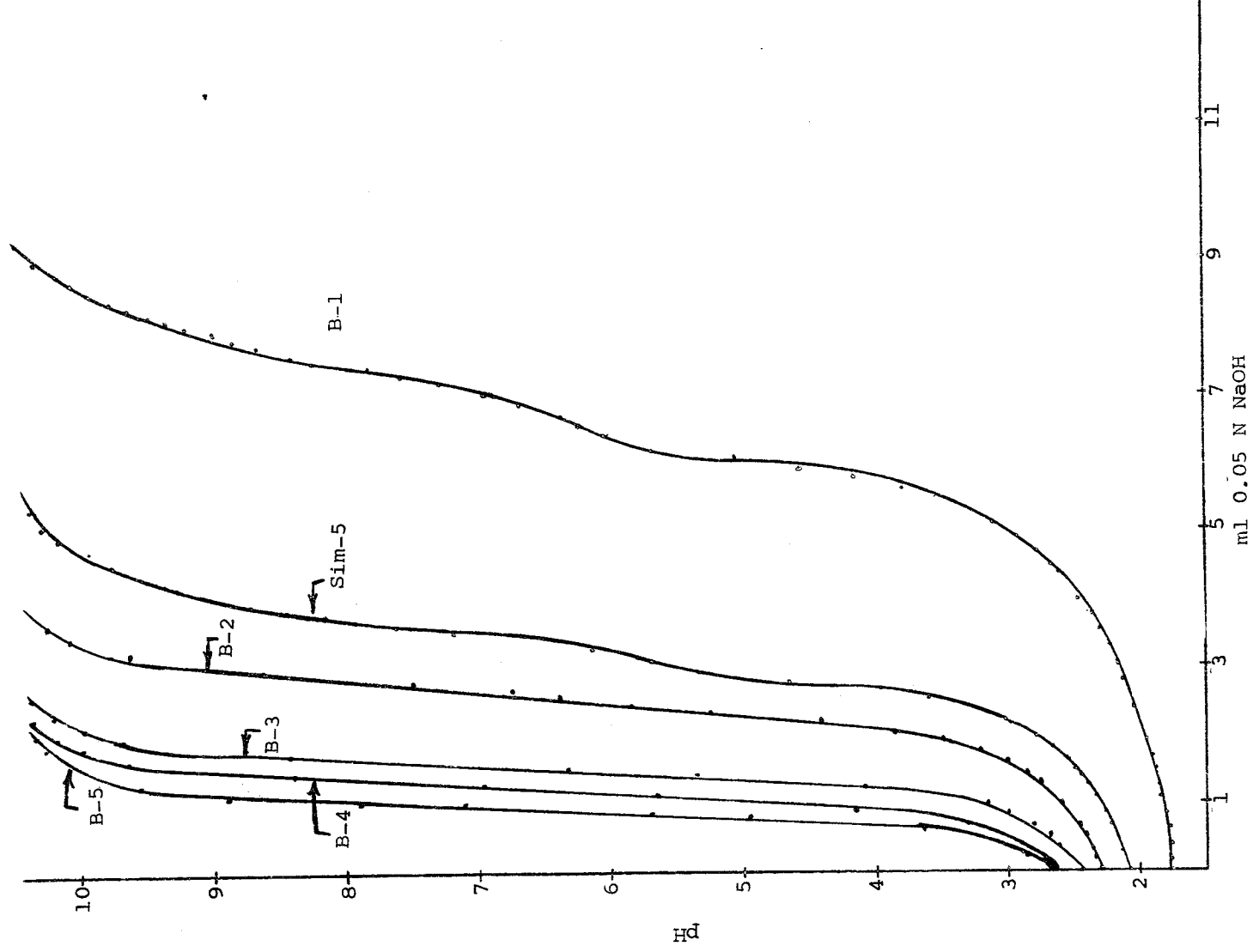


Figure 1
TITRATION CURVES OF FUEL CELL WATER
(10 ml of Water Titrated with 0.05 N NaOH)

As shown in Table 8, the rate of appearance of the organic material is greatly accelerated during the early stages of operation of the cell. Figure 1 shows that the initial water sample (B-1) contributed to 53% of the stronger acid and to 72% of the weaker acid in the base titration curve. The combined contribution of B-1 and B-2, the first 40% of the cell output (10 gal), contributed to 83% of the total titratable acid content, 66% of the total inorganic residue, and over 63% of the organic residue of the total sample.

These data indicate that the purification system will be subjected to much greater concentrations of organic material per unit of time than those that have been screened in any of our total effluent studies. Accordingly, the leakage rates calculated for our batch screening studies are not representative of the in situ operation of the unit. In all probability, the higher concentration of the organic material in the early stages of water output will yield a much higher leakage rate, and if breakthrough does occur, it will occur very early in the flight schedule.

This problem can be circumvented in several ways; however, the final answer involves the flexibility of the vehicle itself. For example, one method would be to divert a certain percentage of the initial water supply from the purification system for storage or vent it completely, depending on the water requirements of the vehicle occupants. An automatic switching device based on pH, conductivity, color, or time could be incorporated

to ensure that the ion-exchange column is not swamped with high levels of organic and inorganic material early in flight. Such high levels could cause immediate breakdown in water quality.

Another method would be to increase the total weight of resin employed in the system. Such an increase would obviously require larger cartridges than presently available. Possibly, several cartridges could be arranged in parallel so that the total load is shared. Arranging the cartridges in parallel should be more convenient from an engineering standpoint, since it would require only an increase in the number of cartridges used. The total weight penalty imposed by this method can be compared with that of the automatic sensing technique to determine the relative merits of the two alternatives. If the total water output of the cell (27 gal) is absolutely essential to sustain the vehicle occupants, the latter method is required and the weight penalty fixed.

The use of a charcoal bed in the final resin system has been completely omitted from this discussion because initially the charcoal was employed solely for the purpose of retaining hydroquinones, which were not being efficiently removed by IRA-68. During the later studies, involving the use of IRA-904, the hydroquinones were removed along with the other organic material just as effectively. Therefore the use of charcoal was not warranted.

V. CONCLUSIONS

A water purification system based on ion-exchange chromatography capable of producing a potable water supply has been developed. As mentioned previously, however, variation in the quality of the fuel cell effluent could alter the efficiency and retention characteristics of this bed system. Recent studies conducted on the GT-5 water samples alone revealed an entirely new requirement for the operational performance of the purification system. This requirement, which was not evident until the flight of GT-5, involves the nonuniform rate of contaminant generation and possible early column loading. The recommendations for the ion-exchange system described herein are based on total or batch water samples rather than sequential output fractions. Of practical significance is the fact that, regardless of the generation rate, if the contaminants are similar, the resin beds screened are still applicable and only alterations of the ratios and orientations would require screening.

Alternative methods for increasing the life and efficiency of the purification system by (1) discarding early heavily contaminated water, (2) incorporating sensing devices for quality control, or (3) increasing total bed weights are reasonable. The final decision on such changes must be made according to the limitations of weight, power, and available space within the vehicle.

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